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PORTLAND CEMENT PASTE I: DENSITY AND
HELIUM FLOW MEASUREMENTS

by R. F. Feldman and V. S. Ramachandran

ANALYZED

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MICROSTRUCTURE OF CALCIUM HYDROXIDE DEPLETED PORTLAND CEMENT PASTE
I: DENSITY AND HELIUM FLOW MEASUREMENTS

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ABSTRACT

Hydrated portland cement contains both free and combined Ca(OH)_2 together with C-S-H. Removal of the Ca(OH)_2 in controlled amounts, first by leaching with an aqueous solution of Ca(OH)_2 and then with water, allows the role of C-S-H to be studied. Helium pycnometric and inflow measurements were made on unleached, leached, and over-leached material. Leaching of the free Ca(OH)_2 did not alter the C-S-H material and did not change any physical properties. Possible engulfing of C-S-H by Ca(OH)_2 is not effective in preventing helium or water flow. Overleaching to the extent that 50% of the CaO was removed from the cement broke down CaO_2 sheets, causing ready access of helium to collapsed interlayer positions. Evidence of a change in the orientation of interlayer water was observed.

RÉSUMÉ

Le ciment portland hydraté contient à la fois du Ca(OH)_2 libre et du Ca(OH)_2 combiné au H-S-C. Le retrait de Ca(OH)_2 en quantités déterminées, en lessivant d'abord avec une solution aqueuse de Ca(OH)_2 puis avec de l'eau, permet d'étudier le rôle du H-S-C. On a pris des mesures pycnométriques d'hélium et d'afflux d'hélium sur des matériaux non-lessivé, lessivé et surlessivé. Le lessivage du Ca(OH)_2 n'a pas modifié le matériau de H-S-C et n'a changé aucune propriété physique. L'engloutissement éventuel du H-S-C par le Ca(OH)_2 n'empêche pas l'afflux d'hélium ou d'eau. En surlessivant de façon à retirer 50% du CaO contenu dans le ciment, on a créé un affaïssement des plaques de CaO_2 , ce qui a facilité l'infiltration d'hélium jusqu'aux couches intermédiaires. On a remarqué un changement dans l'orientation de l'eau des couches intermédiaires.

Introduction

The role of the various phases of hydrated portland cement paste has been the subject of much study and debate (1-3). The C-S-H gel of the cement paste is considered to be of primary importance with regard to the development of both strength and durability. Study of the microstructure of C-S-H

gel presents difficulties because large amounts of Ca(OH)_2 can engulf the C-S-H gel. A study of its role therefore requires removal of Ca(OH)_2 without affecting the C-S-H phase.

C-S-H material itself is in a malformed state both physically and chemically, and for clarifying its structure and the mechanism of strength development it is an advantage to follow changes that occur by gradual breakdown of the material in a step-wise manner. It may thus be possible to assign some of the properties of the C-S-H gel to specific parts of its composition or structure.

In the present study free Ca(OH)_2 was selectively removed from the portland cement paste; this was followed by removal of portions of the Ca^{++} ions or CaO_2 units combined in the C-S-H gel structure. Helium pycnometric and helium inflow measurements were made of the Ca(OH)_2 -depleted residue.

Experimental

Materials

Portland cement, Type I, of the following composition was used: $\text{C}_3\text{S} = 51.5\%$, $\text{C}_2\text{S} = 19.8\%$, $\text{C}_3\text{A} = 12.8\%$ and $\text{C}_4\text{AF} = 6.6\%$. The cement was hydrated at 0.4 and 0.5 w/c (water-to-cement ratio) for 14 years.

Extraction of Ca(OH)_2

Discs 0.64 and 1.0 mm thick were cut from cylinders prepared by hydration of portland cement. They were placed in a vessel and exposed to a large volume of aqueous solution containing 9.5 mmol/L of CaO for removal of free lime (4). For removal of lime from the C-S-H phase (overleaching) they were placed in a large volume of double-distilled water for six months. Slicing and extraction were carried out in a CO_2 -free atmosphere.

Analysis

The method of analysis for Ca(OH)_2 was that described by Ramachandran (4). A differential scanning calorimetric (DSC) cell supplied as a module to a DuPont 990 thermal analysis system was used to obtain thermograms from room temperature to 550°C . In each experiment 20 mg of sample was heated in air at a rate of $10^\circ\text{C}/\text{min}$. For calibration purposes Ca(OH)_2 of known purity was mixed with C_3S in different proportions and endothermal peak areas were plotted against Ca(OH)_2 concentrations. When the peak for Ca(OH)_2 disappeared, it was considered that all the free lime had been removed.

Helium comparison pycnometry and helium inflow

The apparatus and procedure for helium flow measurements have been described in previous papers (5-7). The rate of helium inflow into the sample was measured by pycnometer for 40 h, then density of the material was measured. The technique uses the gas laws and the ideal gas assumption for calculating the solid volume of a sample. Interlayer spaces or very small or partially entrapped spaces that might cause a delayed flow of helium into the sample were considered in the calculations either as part of the solid or as pores.

General Procedure

Thin disc specimens of hydrated portland cement were leached in Ca(OH)_2 solution until all the free Ca(OH)_2 was removed. This was determined by the DSC technique. A free-lime content of 17.75% by weight of sample (based on D-dried unleached state) was removed. Two other samples (w/c, 0.4 and 0.5) were leached in double-distilled water. The 0.5 w/c sample was reduced by 30% by weight of the D-dried unleached sample and the 0.4 w/c sample by 32.75%.

Helium flow and density were measured at different moisture contents, starting from 11% RH condition. Moisture was removed by evacuation alone and, finally, by heating at increasing temperatures and for different periods of time.

Results

Helium Flow

The helium flow curves (volume as a function of time) for the leached sample (wherein only free lime was removed) of hydrated portland cement paste ($w/c = 0.5$) are presented in Fig. 1, and the curves for the overleached sample of the same water-to-cement ratio in Fig. 2. The volume of helium is plotted on the basis of 100 g of unleached sample at 11% RH; the weight loss from 11% RH is also presented on the basis of 100 g of unleached sample at 11% RH. The curves for the leached sample are similar to those found previously for unleached hydrated portland cement and hydrated C_3S (5,6), showing the typical three types observed. These curves have been explained by the progressive collapse that occurs in the structure when interlayer water is removed. Figure 3 shows how helium inflow changes with water removal; the volume of helium that flows into the sample during the first 40 h is plotted as a function of moisture loss (relative to the 11% RH condition) for the leached, overleached (w/c of 0.4 and 0.5) and unleached (w/c of 0.6) specimens. The leached and unleached specimens show somewhat similar results, both demonstrating an abrupt decrease of helium inflow at about 7% weight loss; a total of 9.3 and 10% weight was removed from the two specimens, respectively. The curves for the two overleached samples are very similar to each other, but different from those of the leached and unleached samples. Both show that helium flow increases as water is removed. This is

FIG. 1

Helium inflow in leached cement paste, $w/c = 0.5$

illustrated by the fact that the helium flow curves in Fig. 2 are mainly Type I, as defined previously (5), and show less evidence of Type II behaviour than was found for the leached specimens (Fig. 1).

Solid Volume

Solid volume was measured by the helium comparison pycnometer at different moisture content levels. A plot of the change in volume, as a percentage of each specimen at the 11% RH condition, against weight change is presented in Fig. 4. The volume changes of the leached and overleached specimens are 13 and 16.3%, respectively, while the unleached specimen changed by 12.3%. When

FIG. 2

Helium inflow overleached cement paste, w/c = 0.5

FIG. 3
Helium inflow at 40 h as a function of weight loss for leached cement paste

FIG. 4
Plot of $\Delta V/V$, % at 11% relative humidity as a function of weight loss

the volume changes are plotted on the basis of 100 g of unleached sample at 11% RH, the difference between the specimens is relatively small. The volume change for the overleached specimens indicates that the removal of water involves a collapse of the structure of the material similar to that occurring in the unleached and leached specimens, although this is not indicated by the curves displaying the rate of helium inflow (Fig. 2).

Computation of the term " $\Delta V - \Delta D$ " (at equilibrium, the space occupied by water before removal) can be readily made using these results. Decrease in volume of solid gives a negative ΔV , while increase in "total helium inflow," ΔD , after 40 h relative to the 11% RH condition, gives a positive ΔD . The term $\Delta V - \Delta D$ plotted against weight loss (based on unleached weight at 11% RH) is presented in Fig. 5 for the overleached and leached specimens. A linear plot results for both overleached specimens over the entire weight loss range, and up to 10.9% weight loss for the $w/c = 0.4$ specimen. Linear regression analysis gives straight lines, with a significance in the 0.99 level for the correlation. If all assumptions made in the development of this term (5) are correct and helium fills all the spaces vacated by water molecules, the inverse of the slope of the line yields the density of water, viz., 1.45 ± 0.04 and 1.48 ± 0.09 g/cm³ for the overleached sample made at a $w/c = 0.5$ and 0.4 , respectively, and 1.18 ± 0.06 g/cm³ for the leached paste. The latter value compares with 1.27 ± 0.08 g/cm³ for unleached paste specimens reported previously (5).

The linear portion of the curve for the leached specimen terminates at 6.75% weight loss, as compared with about 6.0% for unleached specimens (5);

FIG. 5

Plot of $\Delta V - \Delta D$ as a function of weight loss

this point coincides with the abrupt decrease in the amount of helium inflow shown in Fig. 3. The overleached specimens show no such behaviour. The collapse of interlayer spaces on removal of water from them was used previously (5,6) to explain the abrupt decrease in helium inflow; there appears to be no such abrupt change in the overleached specimens, but volume change measurements discussed above indicate that such a collapse still occurs.

Density Measurement

The densities of the unleached, leached and overleached specimens, $w/c = 0.5$, are presented in Fig. 6. They are plotted as a function of water loss from the 11% RH condition, based on the unleached weight at 11% RH. The calculation includes the vacated interlayer space as solid volume. The curves for the unleached and leached specimens are similar, but since the density of $\text{Ca}(\text{OH})_2$ is 2.24 g/cm^3 , similar to the values of both specimens, removal of the $\text{Ca}(\text{OH})_2$ should not alter density if the effect is merely additive. On the other hand, overleaching seems to involve other factors since the resulting density is significantly higher. The result for the $w/c = 0.4$ specimens differs, however, in that w/c for the overleached is less than for the unleached; the closer packing of the latter sample and the higher CaO/SiO_2 ratio of the C-S-H formed at $w/c = 0.4$ may be responsible for this effect.

The results when density is computed with the helium flow volume, not included as solid, are presented in Fig. 7 for $w/c = 0.5$ and in Fig. 8 for $w/c = 0.4$. Collapse of the interlayer structure, resulting in decrease of helium flow, is evident for both the unleached and leached specimens. The results for the unleached specimen display an abrupt decrease in density

FIG. 6
Relation between density and
weight loss, $w/c = 0.5$

after about 6.8% weight loss; the maximum density achieved was 2.42 g/cm^3 . The leached specimen also displays an abrupt decrease at about 6.8% weight loss, having attained a maximum density of 2.59 g/cm^3 . The explanation given previously (5-7) is that collapse occurs after removal of a certain quantity of interlayer water from the perimeter of the sheets; helium is unable to gain ready access (within 40 h) to the vacated space. In the overleached specimen no such restriction occurs and the density increases monotonically to a value of 2.64 g/cm^3 . The density of the leached specimen is greater than that of the overleached by between 1 and 8% weight loss. This is due to the fact that, as a fraction of its own weight, the overleached specimen contains more water than the leached. Similar effects may be observed for the $w/c = 0.4$ specimen (Fig. 8). In this case the density of the unleached sample attains a value of 2.41 g/cm^3 and the overleached sample, 2.71 g/cm^3 ; the latter is less dense than the unleached sample in the lower weight loss range.

Discussion

Leaching of free Ca(OH)_2 from hydrated portland cement does not greatly alter the physical properties of the C-S-H material. It is apparent that the free Ca(OH)_2 does not engulf large enough amounts of C-S-H as to make it inaccessible to helium, water vapour or nitrogen (8). The helium flow characteristics shown in Fig. 3 for the leached specimen at $w/c = 0.5$ and the unleached specimen at $w/c = 0.6$ are basically similar; work by Daimon (8) has shown that surface areas measured by nitrogen adsorption are not altered by leaching free Ca(OH)_2 .

FIG. 7

Relation between density of cement paste (corrected for helium inflow) and weight loss, $w/c = 0.5$

The density of the d-dried C-S-H formed by hydrating C_3S paste has previously been calculated (6). By assuming the density of retained interlayer water to be 1.25 g/cm^3 , corrections could be made for interlayer space, allowing the density of C-S-H sheets alone to be calculated; after corrections for free $\text{Ca}(\text{OH})_2$, a density of 2.63 g/cm^3 resulted. When similar corrections for interlayer water were made for the leached sample, a density for the sheets of C-S-H was computed as 2.66 g/cm^3 .

The helium inflow characteristics for the overleached specimen change dramatically (Fig. 3), the helium inflow increasing monotonically with weight loss and the helium flow curves, in Fig. 2, conforming to Type I (8). Helium rapidly enters the spaces vacated by water removal, and in no region of the curve does the collapse of interlayer structure entrap space. This is confirmed in the $\Delta V-\Delta D$ plot in Fig. 5, which decreases linearly over the full range of the weight removed; and in the density curves (Figs. 7 and 8) a monotonical increase in density with weight loss to values of 2.64 and 2.71 g/cm^3 for $w/c = 0.5$ and 0.4 , respectively, is recorded. It is clear that the C-S-H structure has been partially destroyed during overleaching. The ideal structure of tobermorite involves sheets of CaO_2 to which silicate dreierkette chains are attached. These units are separated by water molecules and calcium ions. The orientation of the water molecules between the surfaces and around the calcium ions is not known. C-S-H phase can be considered a disoriented form of tobermorite (9). The overleaching will remove much of the CaO_2 sheets from the silicate dreierketten, probably creating many gaps and channels or holes; this explains the helium flow between the dreierketten despite collapse on removal of interlayer water.

The structure and degree of polymerization of the silicate component of the C-S-H will also change during overleaching, although the degree of

FIG. 8
Relation between density
(corrected for helium inflow)
and weight loss, $w/c = 0.4$

polymerization of the silica in C-S-H (10) is not so great as one would expect for a tobermorite structure. Leaching of $\text{Ca}(\text{OH})_2$ would probably stimulate further polymerization, as it does when $\text{Ca}(\text{OH})_2$ is removed from the C-S-H in its reaction with CO_2 (11).

Polymerization of the silica and a change in the concentration of Ca^{++} in the interlayer space could have a significant effect on the forces binding sheets together and in the orientation of interlayer water. The ΔV - ΔD plots in Fig. 5 show that the density of the interlayer changes with overleaching from $1.18 \pm 0.06 \text{ g/cm}^3$ for the leached sample to $1.45 \pm 0.04 \text{ g/cm}^3$ for the $w/c = 0.5$ paste. These results may be significant: the orientation and quantity of water held between the sheets may affect properties such as drying shrinkage and creep greatly.

Conclusions

1. Leaching of free $\text{Ca}(\text{OH})_2$ from hydrated portland cement does not alter the C-S-H phases. The free $\text{Ca}(\text{OH})_2$ does not engulf C-S-H in such a way as to make part of it inaccessible to helium or water vapour.
2. Overleaching that removes about half the CaO content of portland cement produces significant changes in the C-S-H phase. Gaps or channels in the CaO_2 layers enable helium to flow in readily when interlayer water is removed, although the collapse of the layered structure is similar to that of hydrated portland cement.
3. Density changes from $1.18 \pm 0.06 \text{ g/cm}^3$ to $1.45 \pm 0.04 \text{ g/cm}^3$ of the interlayer water owing to overleaching indicate that significant changes may occur in the orientation of this water.

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